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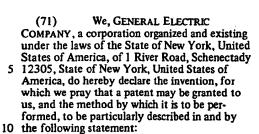
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(54) COMPOSITION AND METHOD FOR IMPROVING THE PROPERTIES OF LIQUIDS

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The present invention relates to compositions and methods for improving the flowing properties of liquids and particularly for reducing friction losses in flowing hydrocarbon fluids. It also concerns a method for producing such compositions by in situ polymerization.

Linear polymers of high molecular weight, including polydiorganosiloxanes as well as various organic polymers are known as effective agents

20 for improving the flow, spreadability, wear resistance and other characteristics of liquids, such as polishes and cosmetics. Also known is their ability to increase the flow of crude oils and refined petroleum products through pipelines.

It is well known that such high polymers as drag reduction additives must be in solution in the liquid e.g., a flowing liquid hydrocarbon, e.g., crude or refined oil, in order to be effective.

However, the practical attainment in the liquid of homogeneous solutions of suitable concentration, typically 10-2000 ppm of polymer, has heretofore presented serious engineering and economic problems. Polymers of the required high molecular weight are hard gums, slow to dissolve and direct injection of bulk polymer is

dissolve, and direct injection of bulk polymer is completely impractical.

To date in laboratory and field tests, with pipeline fluids, it has proven convenient to inject previously prepared "master batch" solutions in

hexane and kerosene. However, at levels of full scale use, which approach millions of pounds of additive annually, serious problems arise in the production, shipment and storage of such solutions.

One basic problem is the very high viscosity of master batch solutions, because of the necessarily high molecular weight of the drag-reducing polymer. Above a concentration limit of about 5 percent, the viscosity becomes so high that such solutions become impractical for injection pumping, and also very difficult to produce at uniform and controlled concentration. The cost of purchase and shipment of such large amounts of solvent in relation to active polymer is a serious burden.

A second basic problem is that the process of dissolving the hard gums ordinarily employed is inherently lengthy and expensive. Agitative intensity must be kept low to avoid shear degradation of the dissolved polymer to shorter chains, because these are ineffective as drag reducers. This requires costly investment in very bulky equipment of unconventional type.

Although it is possible to ship the polymer in bulk and to convert it to master batch at the injection site, typically using part of the pipeline contents as "free" solvent, in practical terms, the number of separate dissolving machines becomes prohibitive. Users strongly prefer instead to employ a formulated product ready for injection, rather than to be encumbered with dissolving operations.

It has previously been proposed that a more convenient drag reduction product might be made by milling bulk high polymer resin into fine particles, which will dissolve more readily. These, however, tend to reagglomerate on standing, and means of preventing reagglomeration have not been found. Further, in all



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processes involving mechanical disintegration of bulk resin, whether or not in the presence of a second, non-solvent liquid phase (for example by milling, colloid milling or homogenizing), there is grave risk of shear degrading the polymer.

According to the present invention there is provided a composition for reducing the fluid flow friction in the transmission of hydrocarbon fluid of viscosity of less than 2000 centipoise at 25°C, said composition comprising

(i) a discontinuous phase comprising particles of not more than 4 microns in diameter of a polymer having a viscosity average molecular weight of at least 500,000 and being a linear hydrocarbon polymer or a polydiorganosiloxane which is ultimately miscible (as herein defined) with a hydrocarbon fluid of viscosity of less than 2000 centipoise at 25°C, and

(ii) a continuous phase of a liquid which is miscible with the same hydrocarbon fluid.

As used herein "ultimately miscible" means that after being mixed with the hydrocarbon fluid in which fluid flow friction is to be reduced, the dispersion in its entirety will ultimately dissolve in the hydrocarbon fluid, but will remain discontinuous for a period sufficient to allow the hydrocarbon fluid to complete one or more operations requiring reduced friction flow.

The new compositions of this invention can have the following advantages:

(1) They can contain as much as 50 percent or more of drag-reduction effective polymer at readily pumpable consistencies.

(2) In preferred cases, and according to one aspect of the invention, the polymer can be formed in situ as the final disperse phase, with very significant elimination of processing steps and degradation hazard.

(3) The laborious operation of dissolving high polymer, and the need for using large volumes of solvent are entirely eliminated.

In addition, they appear to be longer acting than prior art compositions. This seems to result from the fact that under pipeline flow conditions, only dissolved polymer suffers shear degradation; suspended particles are immune. The smallest particles dissolve most rapidly, while larger droplets dissolve more gradually during passage along the pipeline. This results in continuous replenishment of the longest, most effective molecules in solution, directly offsetting any loss due to shear degradation. With adequate control of particle size distribution, benefits approximating those of multiple injection sites along the line can be obtained with the economy of a single injection. This controlled rate of solution principle bears a partial analogy to the 12 hour cold capsule,

which releases medication slowly.

The present invention also provides a process for transmitting a hydrocarbon fluid having a viscosity of less than 2000 centipoise at 25°C through a pipeline with reduced fluid flow

friction, which comprises:

A. mixing with said fluid a composition comprising:

 (i) a continuous phase of a liquid which is different from but miscible with said hydrocarbon fluid, and, dispersed therein,

(ii) a discontinuous phase comprising particles of not more than 4 microns in diameter of a polymer having a viscosity average molecular weight of at least 500,000 and being a linear hydrocarbon polymer or a polydiorganosiloxane, which is ultimately miscible (as herein defined) with said hydrocarbon fluid, the amount of said composition being selected to provide from 10 ppm to 1500 ppm of high molecular weight polymer based on said hydrocarbon fluid; and

B. transmitting the resulting mixture through

a pipeline.

According to another aspect, the present invention provides a process for producing a composition capable of reducing friction losses in flowing hydrocarbon fluids of viscosity of less than 2000 cps at 25°C which process comprises:

(i) dissolving or suspending a monomer capable of forming a polymer or optionally a mixture of monomers capable of forming a copolymer, said polymer or copolymer having a viscosity average molecular weight of at least 500,000 and being a linear hydrocarbon polymer or a polydiorganosiloxane, in a continuous phaseforming liquid which is miscible with a hydrocarbon fluid of viscosity of less than 2000 cps at 25°C; and

(ii) subjecting the monomer or monomers to polymerization conditions so as to produce a discontinuous phase comprising particles of not more than 4 microns in diameter of a polymer or copolymer having a viscosity average molecular weight of at least 500,000 and being a linear hydrocarbon polymer or a polydiorgan-osiloxane and being ultimately miscible (as herein defined) with the same hydrocarbon liquid dispersed in said continuous phase forming liquid.

persed in said continuous phase-forming liquid. Preferably, the monomer will be a silicone 110 precursor, e.g. octamethylcyclotetrasiloxane; a preferred continuous phase-forming liquid is heavy mineral oil or a methylnaphthalene or mixture therof having from one to three methyl groups per molecule. In another preferred feature, 115 the monomer will be polymerized in the presence of a transient catalyst, e.g. tetrabutylphosphonium silanolate, at an elevated temperature, e.g. 50-125°C, preferably 80 ± 10°C, and then the catalyst will be destroyed by heating at a 120 higher temperature, e.g. 125-200°C, preferably at about 150 ± 10°C. Preferred high molecular weight polymers will be polydiorganosiloxanes in which 20 to 100 percent of the organic groups linked to silicon are methyl groups and any remainder are phenyl groups.

In other preferred features, the invention will be used with hydrocarbon fluids comprising crude oil and refined petroleum products, e.g., gasoline, kerosene, distillate fuel oil, jet fuel oil, liquified petroleum gas, pentane, cyclohexane, isooctane, toluene and mixtures thereof.

The high molecular weight resins will be polyhydrocarbons or polydiorganosiloxanes, each having a viscosity average molecular weight of at least 500,000, and preferably above 1 million, up to 40 million. If the drag-reducing polymer is a polyhydrocarbon, preferred liquids which are normally miscible with the hydrocarbon fluids are selected from a monohydric alcohol of from 1 to 16 carbon atoms; a dihydric alcohol of from 7 to 16 carbon atoms; an ester of a mono or polyhydric alcohol of from 1 to 16 carbon atoms and an acid of from 6 to 30 carbon atoms; a polyoxyalkylene dialkyl ether; or a hydrocarbon solution of a second polymer of lower molecular weight polyhydrocarbon. If the drag-reducing polymer is a polydiorganosiloxane, the preferred liquid which is normally miscible with the hydrocarbon fluids is a liquid hydrocarbon oil of average molecular weight of less than about 2000; optionally, but preferably, these compositions will also include a surface active agent comprising a poly(methylalkyl) siloxane fluid.

Factors affecting the consistency of the present drag-reducing compositions are primarily the viscosity of the continuous phase, and also the volume percent of disperse phase, especially when the latter exceeds about 50 percent. For convenience in handling and pumping the continuous phase should generally have a viscosity of less than 2000 cps at 25°C.

The range of compositions embraced by this invention is very broad, extending over both silicone and non-silicone polymers. Illustrative embodiments are:

1. A linear hydrocarbon polymer dispersed in one of the following:

(a) a non-solvent monohydric alcohol of I to 16 carbon atoms;

(b) a non-solvent dihydric alcohol of at least 7 carbon atoms;

(c) a non-solvent ester, e.g., a mixed fatty acid glyceride such as vegetable oil;

(d) a non-solvent polyoxyalkylene dialkyl ether, e.g., tetraethylene glycol dimethyl ether;

(e) a hydrocarbon solution of a second polymer of lower molecular weight and composition dissimilar to the dispersed polymer; and

2. A polydiorganosiloxane dispersed in a non-solvent hydrocarbon, e.g., white mineral oil or an aromatic process oil.

55 To promote physical stability of these compositions, which may be termed oil-in-oil emulsions, it is preferred to incorporate a suitable surfactant material selected for non-interference with the method of preparation and with the drag reduction function. The role of the surfactant is to promote a fine state of sub-division of the disperse phase and to retard its rate of coales-

in the prior art of emulsions in which neither

phase is aqueous. It was not until 1965 that Molau, Journal of Polymer Science A 3(4), 1267-1278 provided a "verification of the existence of oil-in-oil emulsions"

A very few earlier workers disclosed dispersions of polyhydrocarbons or of vegetable oils in non-aqueous continuous phases including glycerol, formamide or ethylene glycol; but the latter are all water-miscible and hydrocarbonimmiscible, and therefore none of these earlier systems would be suggestive of the present discovery.

As has been mentioned, suspensions of linear polydiorganosiloxanes in selected hydrocarbon oils represent one preferred class of the invention. 80 According to this invention, there can be used an in situ polymerization of an initially homogeneous solution of cyclic siloxane(s) in the hydrocarbon oil. The linear polymers thus produced, upon reaching a relatively low polymer stage, separate from the hydrocarbon phase as microscopic droplets. Polymerization continues within these droplets until high molecular weight is reached.

In a preferred silicone-in-hydrocarbon embodi- 90 ment, exemplified hereinafter, a transient catalyst, e.g., tetrabutylphosphonium silanolate is used; the polymerization is run at a conventional temperature range, e.g., 80 ± 5°C. for such catalyst, and after polymerization is complete the catalyst is destroyed by heating to a higher temperature. These materials have superior resistance to degradation during use as drag-reduction agent. Alternatively, the catalyst may be an alkali metal silanolate, typically effective at higher temperatures, and the final suspension may be decatalyzed by addition of suitable trace amounts of soluble acid, e.g., an aliphatic carboxylic acid or a naphthenic acid.

Certain poly(methylalkyl)siloxane fluids chainstopped by trimethylsilyl groups have been found to be effective dispersing agents in the above polydiorganosiloxane-hydrocarbon oil systems, as detailed hereinafter.

As has been mentioned, suspension of linear 110 polyhydrocarbons in selected liquids as the continuous phase represent another preferred class of the invention. The polyhydrocarbons can be any of the drag-reducing polyhydrocarbons of the prior art, such as polyisobutene, polyisoprene, 115 polybutadiene, ethylenepropylene copolymers or olefin-styrene copolymers, or they may be linear polyhydrocarbons such as isoprenebutadiene random copolymers, polyisobutenepolybutadiene block copolymers, etc., provided · 120 only that the viscosity average molecular weight is at least 500,000 and preferably one million or

In general, the continuous phase media of this class are liquids which are (1) non-solvents for the selected high molecular weight linear polyhydrocarbon, and (2) miscible with liquid hydrocarbons of average molecular weight less Surprisingly, there is almost a complete absence than about 2000. A preferred group of media which meet these criteria are aliphatic mono-

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hydric alcohols of 1 to 16 carbon atoms, e.g., methanol, hexanol, isooctanol, decanol and hexadecanol. Another preferred group comprises selected esters meeting the above criteria, for 5 example mixed fatty acid glycerides such as cottonseed oil, peanut oil, and soybean oil. Low-cost, inedible grades of these oils are satisfactory in the present invention.

In general, as will be understood by those 10 skilled in this art, simple liquid hydrocarbons or refined petroleum oils within the useful viscosity range (<2000 cps), such as those detailed in the polysiloxane examples hereinafter, tend to dissolve linear polyhydrocarbons, and are therefore unsatisfactory as continuous phases because extremely viscous solutions are formed rather than the desired two-phase suspensions. Exceptions may exist where the solubility parameters of polymer and liquid differ by an unusually large amount. However, without recourse to such exceptions, a wide range of low-cost hydrocarbon liquids and oils can nevertheless be used, by taking advantage of the well-known phenomenon of mutual exclusion from solution of dissimilar polymers. Specifically, systems comprising three components, as follows: (1) linear polyhydrocarbon, >MW 500,000,

(2) low polymer, MW 50,000, $\delta = y$ (3) oil, MW 900, $\delta = z$

Where δ represents the solubility parameter and x, y and z are the particular values of the solubility parameters, where x and y are substantially dissimilar, and y and z are much closer to each other than they are to x, exist as a stable two-phase system in which there is

(i) a continuous phase containing all of the low polymer and nearly all of the oil, and

(ii) a disperse phase containing all of the high polymer and a small part of the oil.

In such a system, the low polymer (2) need not be a polyhydrocarbon. It can be a chemically different low polymer, such as a polyvinyl acetate, a polyoxyalkylene ether or a polysiloxane.

In order to promote and maintain a fine dispersion, a practical suspension of this general model will also preferably contain a surfactant, chosen for preferential compatability with the oil-low polymer phase in order to favor the latter as the continuous phase (Bancroft's Rule).

In the practice of the method of the present invention, the composition is intermixed with the liquid to be transported, and the liquid is pumped and transferred in conventional manners, as described in the patents above-mentioned. While significant reduction in frictional losses are observed using polymers having a viscosity average molecular weight of as low as 500,000, it is preferred that the high polymers have a molecular weight in the range of from about 1 million to about 40 million and preferably in the range of from about 7 million to about 20 million. The compositions afford effective reductions in drag when the polymer component dissolves in the hydrocarbon fluid to provide

a concentration of at least 5 parts per million (ppm), although they are preferably employed in the range of from 10 ppm to 1500 ppm. The optimum amount will vary, depending on the molecular weight of the polymer, the nature of the hydrocarbon fluid and the flow conditions of the fluid. Those skilled in the art are well aware of these effects. The following examples are illustrative of the present invention. They are not intended to limit the scope of the invention in any manner whatsoever. EXAMPLE 1

Thirty-six grams of extra heavy white mineral oil, 27.5 g. of octamethylcyclotetrasiloxane, and 0.5 g. of trimethylsilyl-stopped poly(methylalkyl). 80 siloxane (surfactant, General Electric Co. SF-1100) are heated in an oil bath and stirred under nitrogen at a pot temperature of 133°C. for 1 hour for azeotropic drying, during which 1.2 g. of the (Me2SiO)4 is vaporized from the 85 flask. The bath temperature is then reduced to 95°C. and 10 drops of Bu₄P silanolate catalyst is added to the clear mixture. Within 10 minutes haze is seen indicating separation of a polydimethylsiloxane phase. Thereafter, the opacity and the amount of siloxane disperse phase increases rapidly. After 2.1 hours at 94-95°C. a sample is taken via hypodermic syringe without needle. The intrinsic viscosity in toluene at 25.0°C. is 1.45 dl/g., viscosity average molecular weight 800,000.

After 4 days of aging at room temperature, this suspension is still well dispersed and shows no tendency to agglomerate. Microscopic examination shows that a large proportion of the resin droplets are in the 3—4 micron diameter range.

The composition upon addition to hydrocarbon fluid, in an amount to provide from 10 to 1500 ppm of silicone polymer content, is effective to reduce the frictional drag on the fluid upon transfer through a pipeline. EXAMPLE 2

Instead of white mineral oil as in Example 1, an aromatic process oil is used to suspend the polydimethylsiloxane particles. Flexon 391, a commercial product (Exxon Company) sold under the following specifications:

under the following specifications:
Density 0.9745

Viscosity 866 csk at 100°F. 115

Composition, % Aromatics 66.5

Saturates 30.5

Polar compounds 3.0 120

is treated to remove catalyst-reactive impurities by passing a hexane-Flexon 391 mixture through a bed of activated alumina and stripping off the hexane under dry nitrogen. A mixture of 19.14 g, of the purified Flexon oil and 18.00 of (Me₂ SiO)₄ and 0.5 g, of trimethylsilylstopped poly(methylalkyl)siloxane surfactant is azeotroped dry (1.93 g, D₄ distilled) and polymerized as in Example 1. Five minutes after addition of catalyst (20 drops Bu₄ P silanolate)

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at 90° C. a heavy cloud appears. After 4.4 hours at $80 \pm 10^{\circ}$ C. the polymer is a smooth suspension of fine polydimethylsiloxane droplets with a viscosity molecular weight of 960,000.

The composition upon addition to hydrocarbon fluid, in an amount to provide from 10 to 1500 ppm of silicone polymer content, is effective to reduce the frictional drag on the fluid upon transfer through a pipeline.

10 EXAMPLE 3

Instead of white mineral oil as in Example 1, a methylnaphthalene fraction of petroleum origin is used to suspend the polydimethylsiloxane particles. Methylnaphthalene No. 2, a commercial product of Crowley Hydrocarbon Chemicals, Inc., is treated to remove catalyst-reactive impurities by passing it through a bed of activated alumina. A mixture of 16.20 g. of the purified methylnaphthalene, 10.48 g. of

purified methylnaphthalene, 10.48 g. of (Me₂SiO)₄ and 0.2 g. of trimethylsilylstopped poly(methylalkyl)siloxane surfactant is azeotroped dry and polymerized as in Example 1. After 20 hours at 86 ± 4°C., the polymer is a smooth suspension of fine polydimethylsiloxane droplets with a viscosity average molecular weight of 6,690,000.

The composition upon addition to hydrocarbon fluid, in an amount to provide from 10 to 1500 ppm of silicone polymer content, is

effective to reduce the frictional drag on the fluid upon transfer through a pipeline.

A common method of preparing linear polyhydrocarbons is emulsion polymerization of the corresponding olefins, or mixtures thereof. The result is a latex of polyhydrocarbon dispersed in a water-surfactant medium. These are commercially available in a wide variety. While the molecular weights of many commercial latices may be too low for effective drag reduction in general higher molecular weights, in the drag reduction range, are obtainable by suitable modification of polymerization conditions. A nonaqueous suspension for direct use in pipeline hydrocarbon streams is made by replacing the water phase of a latex with a water-soluble, hydrocarbon-soluble organic liquid, as disclosed above. With due consideration of the nature of surfactant agent(s) already present, and possibly the addition of further suitable surfactant, such replacement can be made without substantial coalescence of the emulsion.

A styrene-butadiene copolymer latex (General Aniline and Film Co., GAF1400) 60 percent disperse phase, is blended with two volumes of a 1:1 water-tetraethylene glycol dimethyl ether solution with no visible coagulation or other change. The water is then removed by vacuum distillation to give a dispersion of butadienestyrene copolymer in tetraethylene glycol dimethyl ether, both phases of which are soluble in distillate fuel oil, gasoline, and other liquid hydrocarbons.

EXAMPLE 4

The composition upon addition to hydrocarbon fluid, in an amount to provide from 10 to 1500 ppm of resin copolymer content, is effective to reduce the frictional drag on the fluid upon transfer through a pipeline.

The procedure is repeated with water based latices of polyisobutylene, polyisoprene, polybutadiene and polymers and copolymers of ethylene, proylene and alpha olefins of from 4 to 20 carbon atoms. There are obtained drag reducing compositions according to this invention in which the liquid phase is tetraethylene glycol dimethyl ether.

EXAMPLE 5

By conventional methods, e.g., that of U.S. Patent 3,635,863, an emulsion is formed using a vegetable oil (e.g., cottonseed oil, peanut oil) plus surfactant as continuous phase, and the preformed polymer-in-water styrene-butadiene copolymer latices of Example 4 as disperse phase. The result is a three-phase, oil-in-water-in-oil-emulsion. The water is then removed in vacuo leaving a very fine polymer-in-oil suspension suitable for drag reduction in pipelines.

The procedure is repeated with water-based latices of polyisobutylene, polyisoprene, polybutadiene and polymers and copolymers of ethylene, proylene and alpha olefins of from 4 to 20 carbon atoms. Substantially the same results are obtained.

EXAMPLE 6

EXAMPLE 6
Polyisobutylene (m.w. 10,000,000) is dissolved in methylene chloride and mixed with hexadecanol to provide a homogeneous solution. Selective distillation of the methylene chloride leaves a suspension of fine particles of polyisobutylene in hexadecanol which is suitable for use as a drag reducing composition according to this invention. The procedure is repeated, adding a small amount of a surface active agent. A drag reducing composition according to this invention is formed.

EXAMPLE 7

Polyisobutylene (m.w. 10,000,000) is dissolved in kerosene and mixed with a kerosene solution of a polyalkylene oxide (m.w. 10,000–200,000) and a soluble surfactant. The resulting dispersion is concentrated by distillation at reduced pressure and provides an efficiently transportable drag reducing composition according to the present invention.

An ethylene-propylene copolymer (m.w. 1,000,000) is prepared as a dispersion in pentane by using a catalyst comprising a trialkylaluminum and vanadium chloride with an olefin 120 feed containing 20 to 75 mole % ethylene. This dispersion is suitable for use directly, or with an optional surfactant, as a drag reducing polyhydrocarbon according to this invention.

While the above detailed examples describe 125

While the above detailed examples describe useful compositions according to this invention, many obvious variations will suggest themselves to those skilled in this art. The polydimethylsiloxane resins can be replaced in whole or in part with polymethylphenyl or polydiphenyl-

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siloxane unit-containing resins. Suitable surfactants can comprise tall oil, red oil, and commercial anionic and cationic surfactants such as Alamine, Aliquat 21, Priminox 10, Primene JMT, Redicote 5 2323, all used in the weight percent range of from 0.10 to 3% by weight. WHAT WE CLAIM IS:

1. A composition for reducing the fluid flow friction in the transmission of a hydrocarbon 10 fluid of viscosity of less than 2000 centipoise at 25°C, said composition comprising:

(i) a discontinuous phase comprising particles of not more than 4 microns in diameter of a polymer having a viscosity average molecular 15 weight of at least 500,000 and being a linear hydrocarbon polymer or a polydiorganosiloxane, which is ultimately miscible (as herein defined) with a hydrocarbon fluid of viscosity of less than 2000 centipoise at 25 °C.

(ii) a continuous phase of a liquid which is miscible with the same hydrocarbon fluid.

2. A composition as claimed in Claim 1 which also includes:

(iii) a surface active agent to allow the main-25 tenance of (i) as the continuous phase.

3. A composition as claimed in Claim 2 wherein the surface active agent is poly(methyl alkyl) siloxane fluid.

4. A composition comprising: (1) a hydrocarbon fluid of viscosity of less

than 2000 centipoise at 25°C;

(2) from 10 ppm to 1500 ppm, based on the hydrocarbon fluid particles of not more than 4 microns in diameter of a fluid flow friction 35 reducing polymer having a viscosity average molecular weight of at least 500,000 and being a linear hydrocarbon polymer or a polydiorganosiloxane, which is ultimately miscible (as herein defined) with said hydrocarbon fluid; and

(3) a liquid which is different from, but miscible with said hydrocarbon fluid and immiscible with said polymer.

5. A composition as claimed in Claim 4, which also includes:

(4) a surface active agent which is capable in the absence of the hydrocarbon fluid (1) of maintaining the high molecular weight fluid flow friction reducing polymer (2) and the polymer-immiscible liquid (3) in the form of an oil in oil emulsion in which the polymer immiscible liquid (3) forms the continuous

6. A composition as claimed in any one of Claims 1 to 4, wherein the hydrocarbon fluid is 55 a crude oil or a refined petroleum product.

7. A composition as claimed in Claim 6 wherein said hydrocarbon fluid is a refined petroleum product selected from a gasoline, kerosene, distillate fuel oil, jet fuel oil, liquified petroleum gas, pentane, cyclohexane, isooctane, toluene, and mixtures thereof.

8. A composition as claimed in any one of Claims 1 to 7, wherein said liquid which is miscible with said hydrocarbon fluid is selected from a monohydric alcohol of from 1 to 16

carbon atoms, an ester of a mono or polyhydric alcohol of from 1 to 16 carbon atoms and an acid of from 6 to 30 carbon atoms; a polyoxyalkylene dialkyl ether; or a hydrocarbon solution of a second polymer of lower molecular weight and composition chemically different from that of the high molecular weight polyhydrocarbon when the discontinuous phase is a polyhydrocarbon.

9. A composition as claimed in any one of Claims 1 to 7, wherein said liquid which is miscible with said hydrocarbon fluid is a liquid hydrocarbon oil of average molecular weight of less than 2000, when the discontinuous phase is a polydiorganosiloxane.

10. A process for transmitting a hydrocarbon fluid a viscosity of less than 2000 centipoises at 25°C through a pipeline with a reduced fluid flow friction loss, which comprises:

A. mixing with said fluid a composition comprising:

(i) a continuous phase of a liquid which is different from but miscible with said hydrocarbon fluid, and dispersed therein,

(ii) a discontinuous phase comprising particles of not more than 4 microns in diameter of polymer having a viscosity average molecular weight of at least 500,000 and being a linear hydrocarbon polymer or a polydorganosiloxane, which is ultimately miscible (as herein defined) with said hydrocarbon fluid, the amount of said composition being selected to provide from 10 ppm to 1500 ppm of high molecular weight polymer based on said hydrocarbon fluid; and

B. transmitting the resulting mixture through a pipeline.

11. A process as claimed in Claim 10, wherein said composition also includes:

(iii) a surface active agent to allow the maintenance of (i) as the continuous phase and (ii) as the discontinuous phase.

12. A process as claimed in Claim 7 wherein the surface active agent is poly(methylalkyl) siloxane fluid.

13. A process as claimed in any one of Claims 10 to 12, wherein the hydrocarbon fluid is a crude oil or a refined petroleum product.

14. A process as claimed in Claim 13, wherein said hydrocarbon fluid is a refined petroleum product selected from gasoline, kerosine, distillate 11 fuel oil, jet fuel oil, liquified petroleum gas, pentane, cyclohexane, isooctane, toluene and mixtures thereof.

15. A process as claimed in any one of Claims 10 to 14 wherein said liquid which is miscible with 12 said hydrocarbon fluid is selected from a monohydric alcohol of from 1 to 16 carbon atoms; a dihydric alcohol of from 7 to 16 carbon atoms, an ester of a mono or polyhydric alcohol of from 1 to 16 carbon atoms and an acid of from 6 to 30 carbon atoms; a polyoxyalkylene dialkyl ether; or a hydrocarbon solution of a second polymer of lower molecular weight and composition chemically different from that of the high molecular weight polyhydrocarbon when the

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discontinuous phase is a polyhydrocarbon. 16. A process as claimed in any one of Claims 10 to 15, wherein said liquid which is miscible with said hydrocarbon fluid is a liquid hydro-

5 carbon oil of average molecular weight of less than 2000, when the discontinuous phase is a polydiorganosiloxane.

17. A process for producing a composition capable of reducing friction losses in flowing 10 hydrocarbon fluids of viscosity of less than 2000 centipoise at 25°C which process com-

(i) dissolving or suspending a monomer capable of forming a polymer or optionally a 15 mixture of monomers capable of forming a copolymer, said polymer or copolymer having a viscosity average molecular weight of at least 500,000 and being a linear hydrocarbon polymer or a polydiorganosiloxane, in a continuous

20 phase-forming liquid which is miscible with a hydrocarbon fluid of viscosity of less than

2000 cps at 25°C, and

(ii) subjecting the monomer or monomers to polymerization conditions so as to produce a 25 discontinuous phase comprising particles of not more than 4 microns in diameter of a polymer or copolymer, the polymer or copolymer having a molecular weight of at least 500,000 and being a linear hydrocarbon polymer or a 30 polydiorganosiloxane, and being miscible (as

herein defined) with the same hydrocarbon liquid and dispersed in said continuous phase-forming

18. A process as claimed in Claim 17, wherein 35 said monomer or monomers comprise a silicone polymer precursor.

19. A process as claimed in Claim 17, wherein said silicone precursor is octamethylcyclotetrasiloxane and said continuous phase forming 40 liquid is a heavy mineral oil.

20. A process as claimed in Claim 19, wherein said silicone precursor is octamethylcyclotetrasiloxane and said continuous phase forming liquid is an aromatic process oil.

21. A process as claimed in Claim 20, wherein said silicone precursor is octamethylcyclotetrasiloxane and said continuous phase-forming liquid is a methylnaphthalene or mixture thereof having from one to three methyl groups per molecule.

22. A process as claimed in any one of Claims 17 to 21, wherein the polymer is a polydiorganosiloxane in which 20 to 100 per cent of the organic groups linked to silicon are methyl groups and any remaining groups are phenyl groups.

23. A process as claimed in any one of Claims 17 to 22, wherein said monomer or monomers are polymerised in the presence of a transient catalyst at an elevated temperature and, after polymerisation is complete, the catalyst is destroyed by heating to a higher temperature.

24. A process as claimed in Claim 23, wherein said transient catalyst is tetrabutylphosphonium silanolate.

25. A composition for reducing the fluid flow friction loss as claimed in Claim 1 substantially as hereinbefore described.

26. A process for transmitting a hydrocarbon fluid through a pipeline as claimed in Claim 10 substantially as hereinbefore described.

27. A process as claimed in Claim 17 substantially as hereinbefore described in any one of the examples.

28. A composition when produced by a process as claimed in any one of Claims 17 to

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